

The Third Law of Quantum Thermodynamics in the Presence of Anomalous Couplings*

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The quantum thermodynamic functions of a harmonic oscillator coupled to a heat bath through velocity-dependent coupling are obtained analytically. It is shown that both the free energy and the entropy decay fast with the temperature in relation to that of the usual coupling form. This implies that the velocity-dependent coupling helps to ensure the third law of thermodynamics.

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The third law of thermodynamics carries prominent consequences for quantum mechanics and low-temperature physics. It means that all the thermodynamical quantities vanish when the temperature approaches the absolute zero. Great progress in the thermodynamics attributed to this law has been witnessed in elucidating such problems as why the Carnot engine can never reach 100% efficiency at finite temperatures. Although some unfulfillment may still exist the known deviations from the third law will all be cured by quantum mechanics, quantum statistics and interactions among particles according to common wisdom. In particular, the recent widespread interest in the low-temperature behavior of small systems has highlighted a new angle of viewing the critical role that quantum dissipative environment plays in a virginal physical field of study, namely, quantum thermodynamics, for which the validity of the third law is an unavoidable subject to be elucidated. A rather intriguing result has been found that a strong coupling between system and environment should help to ensure the third law of thermodynamics [1]. This encourages us to consider a further investigation on the influence of various coupling forms upon the thermodynamical functions of quantum dissipative system.

Of all coupling forms of four kinds in the system-plus-reservoir model, the velocity-dependent coupling, practically exists in electromagnetic problems such as superconduction quantum interference device [2, 3, 4] or black-body electromagnetic field [5]. This coupling, in the past, is usually believed to be equivalent to the coordinate-coordinate coupling [2, 3, 4, 5, 6, 7, 8], because the velocity coupling Hamiltonian can be transformed into a very similar Hamiltonian with coordinate coupling instead. Nevertheless, the thermal noises produced by these couplings have different power spectra, especially at low frequency [9, 10, 11]. This provides us a new point of view to understand the specific character of different system-reservoir couplings. So it is of great interest to reinvesti-

gate the third law of thermodynamics of a quantum system coupled to a heat bath through velocity-dependent coupling.

In this paper, we get the analytical expressions of the free energy and the entropy of a quantum oscillator in terms of the quantum generalized Langevin equation, which is easier to be treated than the quantum propagator approach [12] for linear problems. It is shown in all cases that the velocity-dependent coupling exhibits a great effort to ensure the third law of thermodynamics than the coordinate-coordinate coupling.

We start from the generalized Caldeira-Leggett system-plus-reservoir Hamiltonian model [2, 4, 13] in the operator form,

$$\hat{H} = \frac{1}{2m}\hat{p}^2 + \sum_{j=1}^N \left[\frac{1}{2m_j}(\hat{p}_j^2 + m_j^2\omega_j^2\hat{q}_j^2) + g(\hat{x}, \hat{p}, \hat{q}_j, \hat{p}_j) \right] + U(\hat{x}), \quad (1)$$

where $\{\hat{x}, \hat{p}\}$ and $\{\hat{q}_j, \hat{p}_j\}$ are the sets of coordinate and momentum operators of system and bath oscillators, respectively, for which the commutation relations are $[\hat{x}, \hat{p}] = i\hbar$ and $[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}$. The coupling term $g(\hat{x}, \hat{p}, \hat{q}_j, \hat{p}_j)$ reads $-c_j\hat{x}\hat{q}_j + \hat{c}_j^2\hat{x}^2/(2m_j\omega_j^2)$ for the usual coupling between system coordinate and environment coordinates; $-d_{1,j}\hat{x}\hat{p}_j/m_j + d_{1,j}^2\hat{x}^2/2m_j$ or $-d_{2,j}\hat{p}\hat{q}_j/m + d_{2,j}^2\hat{q}_j^2/2m$ for the system coordinate (momentum) and environment momenta (coordinates) coupling; and $-e_j\hat{p}\hat{p}_j/mm_j + e_j^2\hat{p}_j^2/(2mm_j^2)$ for momentum-momenta coupling. Noticing that the coupling terms are so written in order to compensate the coupling induced potential and mass renormalization.

After eliminating the degrees of freedom of heat bath via the Heisenberg equations of motion, we get a quantum generalized Langevin equation (QGLE)

$$m\ddot{\hat{x}} + \int_0^t dt' \gamma(t-t')\dot{\hat{x}}(t') + \partial_{\hat{x}}U(\hat{x}) = \hat{\xi}(t), \quad (2)$$

where $\gamma(t)$ is the memory friction function and $\hat{\xi}(t)$ is the random force operator with zero mean, its correlation obeys the quantum fluctuation-dissipation theorem [14, 15]

$$\langle \hat{\xi}(t)\hat{\xi}(t') \rangle_s = \frac{\beta\hbar}{\pi} \int_0^\infty d\omega J(\omega) \coth\left(\frac{\beta\hbar\omega}{2}\right) \cos(t-t'), \quad (3)$$

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where $\langle \dots \rangle_s$ denotes the quantum symmetric average operation and $\beta = 1/k_B T$ is the inverse temperature.

In order to examine the low-temperature thermodynamical behavior of quantum dissipative system, we consider a quantum harmonic oscillator: $U(\hat{q}) = \frac{1}{2}m\omega_0^2\hat{q}^2$. By using the remarkable formula [5, 16, 17, 18], we write the free energy of the quantum oscillator as

$$F(T) = \frac{1}{\pi} \int_0^\infty d\omega f(\omega, T) \text{Im} \left\{ \frac{d \log \alpha(\omega + i0^+)}{d\omega} \right\}, \quad (4)$$

where $f(\omega, T)$ is the free energy of a single oscillator of frequency ω , given by $f(\omega, T) = k_B T \log[1 - \exp(-\hbar\omega/k_B T)]$ with the zero-point contribution $\hbar\omega/2$ being omitted. While $\alpha(\omega)$ denotes the generalized susceptibility which can be got from Eq. (2). Thus the expression of entropy of the quantum oscillator is given by

$$S(T) = -\frac{\partial F(T)}{\partial T}. \quad (5)$$

Since the function $f(\omega, T)$ in Eq. (4) vanishes exponentially for $\omega \gg k_B T/\hbar$, thus as $T \rightarrow 0$ the integrand is confined to low frequencies and we can explicitly calculate the free energy and then the entropy by expanding the factor multiplying $f(\omega, T)$ in the powers of ω .

For the harmonic potential, the QGLE is linear and its explicit solution is obtained

$$\tilde{x}(\omega) = \alpha(\omega) \tilde{\xi}(\omega), \quad (6)$$

where $\tilde{x}(\omega) = \int_{-\infty}^\infty dt \hat{x}(t) \exp(i\omega t)$ is the Fourier transform of $\hat{x}(t)$ and similarly noting is true for $\tilde{\xi}(\omega)$. The explicit expression of the generalized susceptibility in Eq. (6) is given by

$$\alpha(\omega) = [-m\omega^2 - i\omega\tilde{\gamma}(\omega) + m\omega_0^2]^{-1}. \quad (7)$$

First, let us consider the usual case of the system's coordinate coupled to the coordinates of the heat bath. Experimentally, this type of coupling can be realized in a RLC electric circuit driven by a Gaussian white noise. Assuming that the power spectrum of the bath oscillators has a harmonic form, namely, the spectrum has a narrow Lorentzian distribution with the peak centered at a finite frequency. The Fourier transform of the memory friction function is

$$\tilde{\gamma}(\omega) = \frac{2m\gamma_0\Omega^4}{\Gamma^2\omega^2 + (\Omega^2 - \omega^2)^2}, \quad (8)$$

where γ_0 denotes the Markovian friction strength of the system, Γ and Ω are the damping and frequency parameters of the Gaussian noise, respectively. With this the response function, Eq. (7) becomes

$$\alpha(\omega) = \left[-m\omega^2 - \frac{2i\omega m\gamma_0\Omega^4}{\Gamma^2\omega^2 + (\Omega^2 - \omega^2)^2} + m\omega_0^2 \right]^{-1}, \quad (9)$$

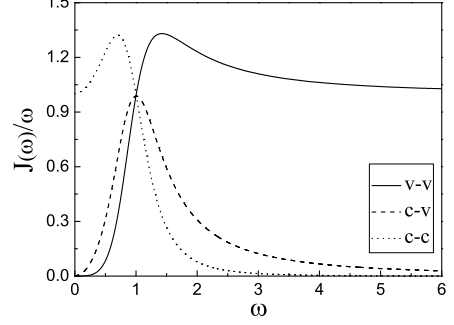


FIG. 1: The power spectra of the noise for the couplings of three kinds: the coordinate-coordinate (c-c), coordinate-velocity (c-v), and velocity-velocity (v-v) couplings, where dimensionless parameters such as $m = 1.0$ and $\gamma_0 = 1.0$ are used as well as $\Gamma = \Omega = 1.0$.

and thus the term appearing in Eq. (4) in the low-frequency limit is written as

$$\begin{aligned} & \text{Im} \left\{ \frac{d \log \alpha(\omega)}{d\omega} \right\} \\ &= \frac{2\gamma_0\Omega^4[5\omega^6 + 3(\Gamma^2 - (\omega_0^2 + 2\Omega^2)\omega^4)]}{(\omega_0^2 - \omega^2)^2(\Gamma^2\omega^2 + (\Omega^2 - \omega^2)^2) + 4\gamma_0^2\omega^2\Omega^8} \\ & - \frac{2\gamma_0\Omega^4[(\Gamma^2 - \Omega^2(\Omega^2 + 2\omega_0^2))\omega^2 - \Omega^4\omega_0^2]}{(\omega_0^2 - \omega^2)^2(\Gamma^2\omega^2 + (\Omega^2 - \omega^2)^2) + 4\gamma_0^2\omega^2\Omega^8} \\ & \cong \frac{2\gamma_0}{\omega_0^2}, \end{aligned} \quad (10)$$

which reduces to the result of Ohmic friction [19, 20]. Hence, we get the expression of the free energy of quantum oscillator at low temperature,

$$\begin{aligned} F(T) &\cong \frac{2\gamma_0 k_B T}{\pi\omega_0^2} \int_0^\infty d\omega \log[1 - \exp(-\hbar\omega/k_B T)] \\ &= -\frac{\pi}{3} \hbar\gamma_0 \left(\frac{k_B T}{\hbar\omega_0} \right)^2. \end{aligned} \quad (11)$$

The entropy thus reads

$$S(T) = -\frac{\partial F(T)}{\partial T} = \frac{2\pi}{3} \gamma_0 \left(\frac{k_B^2 T}{\hbar\omega_0^2} \right). \quad (12)$$

So we have got as $T \rightarrow 0$, $S(T)$ vanishes principle to T , in perfect conformity with the third law of thermodynamics and the linear decay behavior of the entropy is in accordance with the usual case of Ohmic friction.

Secondly, we consider the anomalous case of the first kind for the coordinate (velocity) of the system coupled to the velocities (coordinates) of the heat bath. The spectrum of noise produced by this coupling is shown in Fig. 1. Indeed, it differs very much from the normal coordinate-coordinate coupling [9, 10, 21, 22]. The

Fourier transform of the corresponding friction kernel function reads

$$\tilde{\gamma}(\omega) = \frac{2m\gamma_0\Gamma^2\omega^2}{\Gamma^2\omega^2 + (\Omega^2 - \omega^2)^2}. \quad (13)$$

In the limit of low temperature, we have

$$\begin{aligned} \text{Im} \left\{ \frac{d \log \alpha(\omega)}{d\omega} \right\} &= \frac{4\gamma_0\Gamma^2\omega[\omega^4(\Gamma^2 - 2(\Omega^2 - \omega^2)) + \omega_0^2(\Omega^4 - \omega^4)]}{(\omega_0^2 - \omega^2)^2(\Gamma^2\omega^2 + (\Omega^2 - \omega^2)^2)^2 + 4\gamma_0^2\Gamma^4\omega^4} \\ &\cong \frac{4\gamma_0\Gamma^2}{\Omega^4\omega_0^2}\omega. \end{aligned} \quad (14)$$

By using Eq. (14), we get the free energy

$$\begin{aligned} F(T) &\cong \frac{4\gamma_0\Gamma^2k_BT}{\pi\Omega^4\omega_0^2} \int_0^\infty d\omega \omega \log[1 - \exp(-\hbar\omega/k_BT)] \\ &= -\frac{4\gamma_0\Gamma^2}{\pi\Omega^4} \hbar\omega_0 \zeta(3) \left(\frac{k_BT}{\hbar\omega_0} \right)^3, \end{aligned} \quad (15)$$

where $\zeta(z) = \sum_{n=1}^\infty \frac{1}{n^z}$ is the Riemann's zeta-function. This also results in a vanishing entropy in the low-temperature limit,

$$S(T) = \frac{12\gamma_0\Gamma^2}{\pi\Omega^4} k_B \zeta(3) \left(\frac{k_BT}{\hbar\omega_0} \right)^2, \quad (16)$$

in agreement with the Nernst's theorem. But the decay behavior of the entropy as a function of the temperature in the presence of velocity-dependent coupling is faster than that of the coordinate-coordinate coupling, as a result of the fact that Eq. (14) has a factor ω whereas the corresponding result of Eq. (10) is independent of the frequency. This is due to, from the point of view of theoretical physics, the velocity-dependent coupling leads the memory friction kernel function to a strong dependence on the frequency, thus greatly changed the thermodynamic character of the system.

Finally, let us consider the anomalous dissipation of the second kind, i.e., the system's velocity is coupled to the velocities of the heat bath, the spectrum of the noise is also shown in Fig. 1. The Fourier transform of the friction kernel function for this coupling reads

$$\tilde{\gamma}(\omega) = \frac{2m\gamma_0\omega^4}{\Gamma^2\omega^2 + (\Omega^2 - \omega^2)^2}. \quad (17)$$

This results in

$$\begin{aligned} \text{Im} \left\{ \frac{d \log \alpha(\omega)}{d\omega} \right\} &= \frac{4\gamma_0\omega^3[\omega^6 - \omega^2(\Omega^4 - (\Gamma^2 - 2\Omega^2)\omega_0^2) + 2\Omega^4\omega_0^2]}{(\omega_0^2 - \omega^2)^2(\Gamma^2\omega^2 + (\Omega^2 - \omega^2)^2)^2 + 4\gamma_0^2\omega^8} \\ &\cong \frac{8\gamma_0}{\Omega^4}\omega^3, \end{aligned} \quad (18)$$

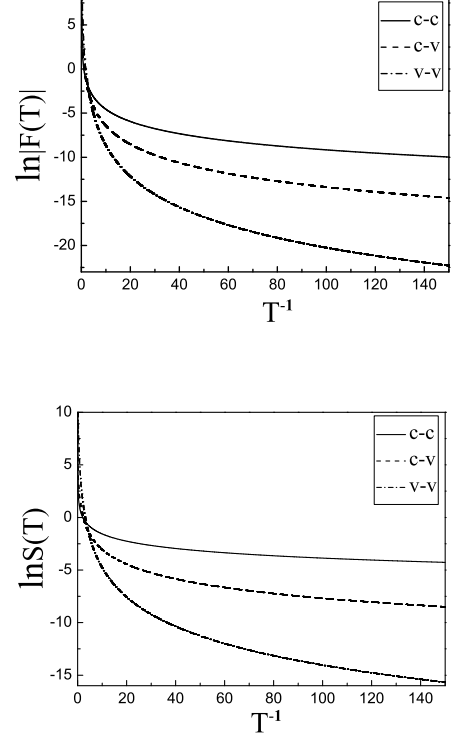


FIG. 2: The free energy and the entropy of the quantum oscillator as functions of the temperature for coupling forms of three kinds with dimensionless parameters $\hbar\omega_0 = k_B = 1.0$ as well as others used in Fig. 1.

in the low-frequency, From which we get the expression of the free energy

$$F(T) = -\frac{48\gamma_0}{\pi\Omega^4} \hbar\omega_0^3 \zeta(5) \left(\frac{k_BT}{\hbar\omega_0} \right)^5, \quad (19)$$

and the entropy is also obtained

$$S(T) = \frac{240\gamma_0}{\pi\Omega^4} k_B \omega_0^2 \zeta(5) \left(\frac{k_BT}{\hbar\omega_0} \right)^4. \quad (20)$$

With this result we conclude again that $S(T) \rightarrow 0$ as $T \rightarrow 0$ of no conflicting with the Nernst's theorem, but a even fast decaying behavior with the temperature for the entropy is found.

For the purpose of explicitly distinguishing the decaying behavior of the free energy and entropies of these three kind of coupling forms, we give out their log-plot illustration in Fig. 2 as a function of the inverse temperature. From which we can see that the thermodynamical functions of velocity-dependent coupling systems exhibit a markedly faster decaying than the coordinate coupling system. This can be easily understood by comparing Eqs. (17) and (13) with Eq. (8), where the friction function of the velocity-dependent coupling is revealed to be strongly

related to the frequency and thus makes the system more quantum mechanically.

In summary, we have obtained the analytical formula of the free energy and the entropy of a quantum oscillator coupled to a heat bath through velocity-dependent coupling form at low temperature. The low-temperature behavior of the thermodynamical functions has been discussed. It is shown that the decay behavior of the thermodynamical functions with the temperature for the anomalous coupling case is faster than that of the usual coordinate-coordinate coupling form when the temperature approaches zero. Rather intriguing is it implied from our study that the fast vanishing entropies of the

velocity-dependent coupling deeply helps to ensure the validity of the third law of thermodynamics at low temperature. The results obtained here for the thermodynamical functions of quantum dissipative system at low-temperature may turn out to be relevant to experiments in nanoscience where one tests the quantum thermodynamics of small systems which are coupled to a structured heat bath. Experimentally, for an example of the system coordinate (velocity) and environment velocities (coordinates) coupling, one can study the interaction between a single electron and the blackbody radiation field where the hamiltonian of the system can be easily considered under the approximation of dipole polarization.

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